

VII.2 Materials System for Intermediate-Temperature SOFC

Uday B. Pal (Primary Contact), Srikanth Gopalan, Wenquan Gong

Department of Manufacturing Engineering, Boston University

15 St. Mary's Street

Brookline, MA 02446

Phone: (617) 353-7708; Fax: (617) 353-5548; E-mail: upal@bu.edu

DOE Project Manager: Lane Wilson

Phone: (304) 285-1336; E-mail: Lane.Wilson@netl.doe.gov

Objectives

- Synthesize and evaluate materials system for intermediate-temperature (600-800°C) solid oxide fuel cell (SOFC).
- Demonstrate feasibility of manufacturing multi-layered SOFC structures utilizing the intermediate-temperature materials system.

Approach

- From literature data, selected the electrolyte, anode, and cathode materials for the intermediate-temperature SOFC system: lanthanum gallate ($\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$, or LSGM) as electrolyte, nickel-gadolinium doped ceria ($\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_{2-x}$, or Ni-GDC) cermet as anode, and LSGM-lanthanum cobaltite ($\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$, or LSCF) composite as cathode.
- Synthesized and confirmed the suitability of the LSGM electrolyte for intermediate-temperature operation.
- Measured the interfacial polarizations of the candidate electrodes for the LSGM electrolyte utilizing impedance spectroscopy.
- After determining optimum electrode composition, structure and thicknesses of the cathode and the anode, complete planar cells will be fabricated and evaluated in terms of their current-voltage (I-V) characteristics and stability.

Accomplishments

- LSGM electrolyte was synthesized. It was found to be stable under fuel cell operating conditions and had the required conductivities to function as an electrolyte for the intermediate-temperature SOFC (Figure 1).
- Optimum active cathode that resulted in the least polarization resistance (0.1 ohm-cm^2 at 800°C) and good thermal expansion match with the LSGM electrode was determined to be a 50-50 volume-% LSCF-LSGM composite having a thickness of 30-40 micrometers.
- Optimum active anode was found to be Ni-GDC cermet having a barrier layer of $\text{Ce}_{0.6}\text{La}_{0.4}\text{O}_{2-x}$ (LDC) between the anode and the LSGM electrolyte.

Future Directions

- Effects of Ni-GDC anode composition, structure and thickness on interfacial polarization will be investigated.
- After determining the composition, structure and thickness of the anode, complete anode-supported planar cells will be fabricated and evaluated at intermediate temperatures in terms of its I-V characteristics and stability.

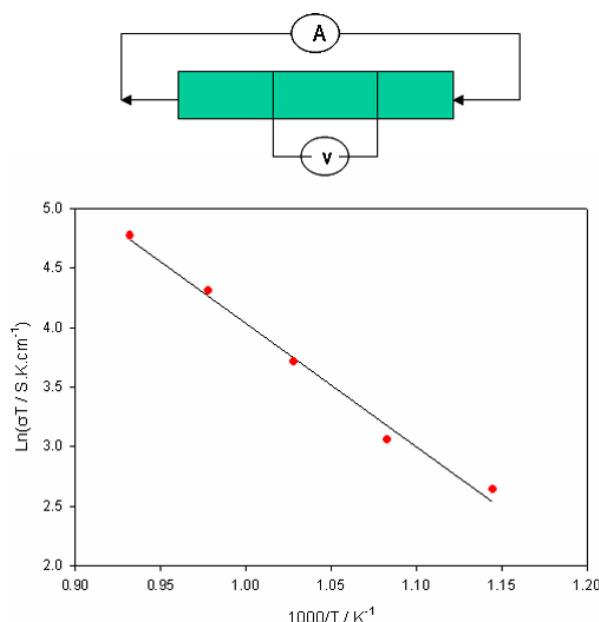


Figure 1. Conductivity of LSGM Electrolyte as a Function of Temperature Measured Using a Four-Probe Technique

Introduction

Solid oxide fuel cells offer the possibility of very high efficiency power generation. They are noiseless, emit far lower quantities of greenhouse gases such as CO_2 compared to conventional power generation systems, and cause virtually zero NO_x and SO_x emissions. They are also fuel cell candidates for enabling the hydrogen economy. Despite their many advantages, SOFC power systems are not yet cost-effective to merit large-scale deployment in the power generation industry. Of the approaches currently being investigated to decrease the cost of SOFCs, improving power density while decreasing operating temperature is perhaps the most promising option. Improvements in power density will result in decreased system size, which in turn will have the effect of decreasing the size of the balance of plant (BOP). Decreasing operating temperature will lead to the deployment of cheaper manifolding and interconnection materials. However, decreasing operating temperature has the effect of increasing all types of polarization losses in the cell. Thus, the simultaneous goals of improving power density and lowering the operating temperature are at odds with each other. Therefore, the focus of recent research is aimed at development of more active electrodes and

more conductive electrolyte materials that can efficiently operate at lower temperatures (600-800°C).

A large fraction of the total polarization losses is known to occur at the electrode-electrolyte interface manifesting itself as the kinetic barrier to charge-transfer reactions. Great advances have been made in reducing electrode polarization related to the charge-transfer reaction through the use of two-phase porous composite electrodes [1-4] and mixed conducting electrodes [5]. Much of this work has been aimed at developing electrodes for SOFCs based on the conventional yttria-stabilized zirconia (YSZ) electrolyte and not on researching a materials system that can be employed to manufacture intermediate-temperature SOFCs. The focus of this work is an investigation of electrode materials for SOFCs based on the perovskite electrolyte $\text{La}_{1-x}\text{Sr}_x\text{Ga}_{1-y}\text{Mg}_y\text{O}_3$ (or LSGM). LSGM has received a lot of interest in recent years after it was first reported by Goodenough et al. [6] to have significantly higher oxygen-ion conductivity than YSZ.

Approach

Powders of the composition $\text{La}_{0.9}\text{Sr}_{0.1}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3$ (LSGM) were synthesized by mixing high-purity precursors of lanthanum carbonate, strontium carbonate, gallium oxide and magnesium oxide in appropriate stoichiometric ratios and calcining at a temperature of 1200°C for 4 hours in air. Electrode materials such as $\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$ (LSM), $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_3$ (LSCF), $\text{Ce}_{0.85}\text{Gd}_{0.15}\text{O}_2$ (GDC), and $\text{Ce}_{0.6}\text{La}_{0.4}\text{O}_2$ (LDC) were also made using a similar procedure.

Calcined and milled LSGM powders at room temperature were die-pressed with 10,000 psi pressure into pellets and sintered in air at 1450°C for 4 hours. The sintered LSGM pellets were 1.4 mm thick and 2 cm in diameter. The LSGM pellets were then all finely ground to a uniform 1 mm thickness using diamond grinding discs. LSM-LSGM, LSCF-LSGM, NiO-GDC, and NiO-LDC composite electrodes were prepared by thoroughly mixing controlled amounts of powders. The electrode powders (LSM, LSM-LSGM, LSCF, LSCF-LSGM, NiO-GDC, NiO-LDC) were each dispersed in *terphenol* solvent to form a paste. The ground LSGM

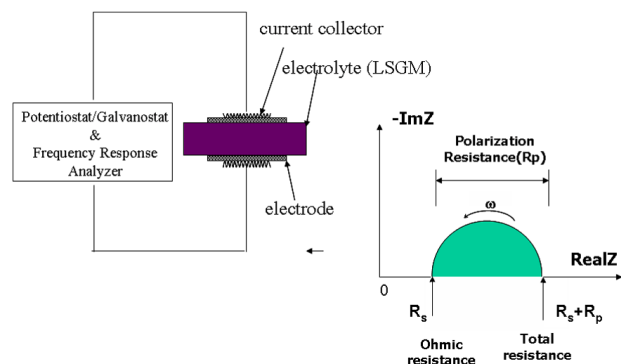


Figure 2. Schematic Diagram of the Experimental Setup Employing Symmetrical Cell for Measuring Electrode Polarization through Impedance Spectroscopy

electrolyte pellets were masked with Scotch™ tape to form an outer ring on both sides, and the electrode pastes were painted smoothly on the open circular surfaces. The painted electrolyte pellets were air-dried, the masks were removed, and the pellets were fired in air at elevated temperature for 2 hours. The firing temperature was 1100°C for all the cathodic samples and 1100-1300°C for the anodic samples. When platinum electrodes were used, commercial platinum paste (6926 Engelhard) was painted over a similarly masked LSGM electrolyte pellet, air-dried, and fired (with masks removed) at 950°C for 2 hrs. All electrodes had the same effective area of around 1.33 cm². For the cathode materials, two pieces of platinum mesh were co-sintered on both electrode surfaces at the same time to act as current collectors. Lead wires of Pt were used to connect the platinum mesh current collectors to the measuring instrument. For the anode materials, Nickel mesh was pressed over the electrode surfaces in a reducing atmosphere, and lead wires of Nickel were used. The experimental setup used for AC impedance characterization is shown in Figure 2. In this setup, the symmetrical cell was exposed to the same oxidizing (cathodic) or reducing (anodic) atmosphere on both sides, and a two-probe configuration was used to measure the impedance spectra. During measurement, a constant flow rate of air was maintained for experiments involving the cathode materials, and a constant flow rate of forming gas, i.e. 95% argon-5% hydrogen bubbled through water at 25°C, was maintained for experiments involving the anode materials. The measurements were made

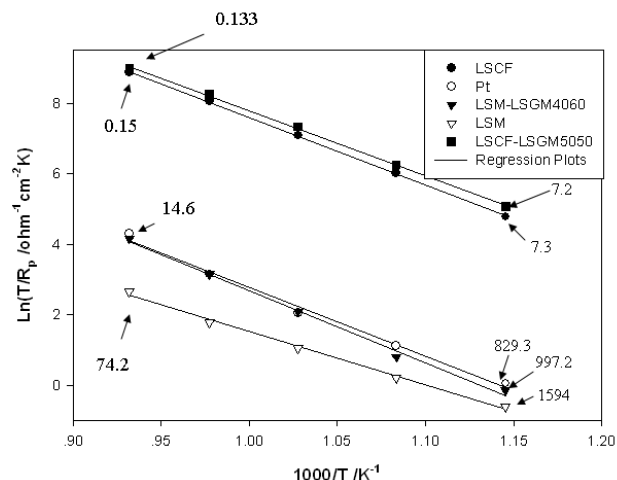


Figure 3. Temperature Dependence of the Polarization Resistance for Various Cathode Materials Measured in Air

in the temperature range of 600 to 800°C by applying a small-amplitude AC voltage (10 mV) to the cell and monitoring the response current as a function of the AC frequency (from 1 mHz to 65 KHz). A plot of the imaginary part of the measured impedance versus the real part reveals details of the individual ohmic and polarization contributions to the total resistance of the cell. After electrochemical testing, the samples were epoxy mounted and polished in cross section; both scanning electron microscopy (SEM) and optical microscopy were used to measure the grain size, porosity and thickness of the electrodes and confirm the consistency of the microstructure.

Results

Among the cathode materials [LSM ($\text{La}_{0.9}\text{Sr}_{0.1}\text{MnO}_3$) and LSCF], the pure LSM electrode had the worst polarization performance. The addition of LSGM electrolyte material to the LSM electrode increased the mixed-conducting boundary with the gas phase and lowered the overall polarization. Although LSM-LSGM composite electrodes are better than just pure LSM, the performance of the best LSM-LSGM (40:60) electrode was similar to that of platinum. Single-phase mixed-conducting LSCF electrode had three orders lower polarization resistance than the LSM-LSGM composite electrodes (Figure 3). Addition of

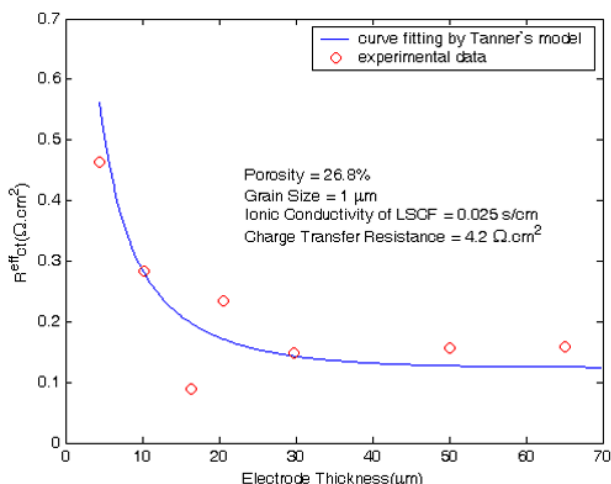


Figure 4. A Plot of Polarization or Charge Transfer Resistance as a Function of Electrode Thickness for Symmetrical LSCF/LSGM/LSCF Cells Measured in Air at 800°C

LSGM to LSCF did not significantly alter (lower) the polarization resistance of the LSCF electrodes (Figure 3). However, a composite LSCF-LSGM electrode is preferred over a plain LSCF electrode in order to match the coefficient of thermal expansion with the LSGM electrolyte. It is also observed that the interfacial polarization resistance of the LSCF electrode decreased asymptotically as the electrode thickness increased. An optimum thickness of 30 to 40 microns is required to minimize the cathodic polarization resistance (Figure 4).

The anode material investigated was Ni-GDC. It was observed that the LSGM electrolyte reacts with the Ni during processing and also at the operating temperature and increased both the ohmic and the polarization resistances. A buffer layer of GDC between the LSGM electrolyte and the Ni-GDC composite anode could not completely prevent this interaction due to lanthanum diffusion when sintering temperature was above 1200°C. The La diffusion also resulted in increasing the ohmic resistance. It is possible to prevent the La diffusion from the LSGM electrolyte by changing the buffer layer from GDC to lanthanum-doped ceria (LDC). It is to be noted that the lanthanum in the LDC does not react with the Ni. Since the ionic conductivity of the LDC is lower than that of GDC, it is desirable to employ a Ni-GDC cermet anode above the LDC barrier layer to lower the polarization resistance.

Effects of Ni-GDC anode composition, structure and thickness on interfacial polarization are being investigated.

Conclusions

Single-phase mixed-conducting LSCF cathodes have much lower polarization resistance than the LSM-LSGM composite cathodes. The polarization resistance of the LSCF cathodes decreases asymptotically as the electrode thickness is increased. Adding LSGM electrolyte material to the LSCF electrode does not improve the cell performance very much, but buffers the larger thermal expansion coefficient of LSCF compared to the LSGM electrolyte. Ni in the anode material reacts with LSGM electrolyte and lowers the overall cell performance. A dense layer of an appropriate buffer oxide (LDC) is needed between the LSGM electrolyte and the Ni-GDC anode.

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FY 2004 Publications/Presentations

1. Wenquan Gong, Srikanth Gopalan and Uday B. Pal, "Polarization Study on Doped Lanthanum Gallate Electrolyte Using Impedance Spectroscopy," *Journal of Materials Engineering and Performance*, Vol. 13, No. 3, June 2004, pp. 274-281.
2. Wenquan Gong, Srikanth Gopalan and Uday B. Pal, "Cathodic Polarization Study on Doped Lanthanum Gallate Electrolyte Using Impedance Spectroscopy," Accepted for Publication in the *Journal of Electroceramics*, March 2004.
3. June 2003, "Cathode Materials for Intermediate Temperature SOFCs," Department of Materials Science and Engineering Graduate Seminar, SUNY Stonybrook.
4. November 2003, "Polarization Study on Doped Lanthanum Gallate Electrolyte Using Impedance Spectroscopy," ASM Fall Meeting, Pittsburgh, PA.
5. June 2004, "Materials System for Intermediate Temperature Solid Oxide Fuel Cell," DOE-UCR Meeting, Pittsburgh, PA.